

PATENT SPECIFICATION

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(54) AQUEOUS COLLOIDAL POLYUREA- URETHANE IONOMER DISPERSIONS

(71) We, TEXTRON INC., a corporation organized and existing under the laws of the State of Delaware, United States of America, of 4201 Genesee Street, Buffalo, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel, stable, aqueous, colloidal dispersions of urea-urethane polymers and to processes for their manufacture. The urea-urethane polymers can be derived by the polyamine extension of isocyanate-terminated, urethane prepolymers which contain tertiary amine-neutralized, carboxylic acid groups. The urea-urethane dispersions of this invention are infinitely dilutable with water and are suitable for use in, for instance, coating compositions and provide water-resistant coatings. The solids of the dispersions are essentially of colloidal size, and the dispersions may be fairly clear or only slightly opaque in appearance.

Urea-urethanes have found widespread use in coatings for fabrics, plastics, wood, metal, and the like, due to their advantageous properties such as their good chemical resistance, abrasion-resistance, toughness, elasticity and durability, and their ability to cure rapidly. Conventionally, urea-urethane coatings have been applied as solutions in, for instance, polar or aromatic hydrocarbon solvents. When the urea-urethanes are of certain types, they may be compatible with aliphatic hydrocarbon solvents. When the coating is being dried, or cured, these solvents vaporize into the

atmosphere as an economic loss and, quite importantly, the vaporous solvents may pollute the atmosphere.

Aqueous, urea-urethane coating compositions are, therefore, particularly desirable due to the low cost and availability of water. Moreover, aqueous coating compositions are advantageous since the evaporation of water into the atmosphere has little, if any, adverse effect on the environment whereas conventionally employed organic solvents may be toxic, odoriferous, or photochemically-sensitive, and thus, may be smog-formers in the daylight atmosphere due to photochemical oxidation. Furthermore, water which is readily available can be used to thin the water-based coating compositions and can be used in clean-up operations. However, urea-urethanes generally are not compatible with water unless special ingredients and/or particular steps of manufacture are employed in their synthesis.

One approach to provide water-dispersible, polyurethane-containing compositions has been through the use of emulsifiers. This procedure generally suffers from the disadvantages that the dispersions are relatively unstable and the resultant films are watersensitive.

Milligan, et al., disclose in U.S. Patent No. 3,412,054, water-dilutable polyurethanes made by incorporating in the urethane polymer, carboxylic acid groups which are reacted with ammonia or amines to provide hydrophilic, carboxylic acid salt groups on the polymer. These ion-containing polymeric materials, or ionomers, are not infinitely dilutable. The patentees disclose the use of an organic cosolvent to permit dilution up to about 5

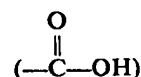
percent resin solids, without the resin separating from the dispersion to a significant extent.

In accordance with the present invention, there are provided stable, aqueous dispersions of urea-urethane polymers that are infinitely dilutable with water, and their solids are essentially colloidal in size. The colloidal dispersions are relatively clear as compared with urethane emulsions or latexes. The appearance of the colloidal dispersions may be from slightly opaque to relatively clear, and may approach, if not reach, the appearance of a solution. The rheological properties of the colloidal dispersions generally resemble those of a true solution. Although the urea-urethane polymer dispersions of this invention are infinitely dilutable with water, they can form cured films having good resistance to water. The urea-urethane polymers may be fully polymerized such that no further reactions need occur during their curing. The films can cure at room temperature, and thus may be described as low energy-consuming materials, and they may be relatively non-polluting since little, if any, organic volatile material need be present in the composition. The urea-urethane compositions of this invention may have a relatively neutral pH, thus a wide selection of pigments can be used without having compatibility problems with the dispersion, and the polymers need not be subjected to high pH conditions which may otherwise tend to promote the hydrolysis of the polymer chain.

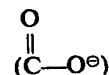
The urea-urethane polymers of this invention can be made by reacting an aqueous dispersion of a tertiary amine-neutralized, isocyanate-terminated urethane prepolymer, derived from a polyisocyanate selected from aliphatic diisocyanates, alicyclic diisocyanates, toluene diisocyanate and xylene diisocyanate, with a polyamine. The isocyanate-terminated urethane prepolymer may be formed by the reaction of diisocyanate and polyol components, at least a portion of which has at least one carboxylic group per molecule which is relatively non-reactive with isocyanates. A portion or all of the carboxylic groups of the urea-urethane is neutralized with tertiary amine groups to provide a polymer which can have a relatively neutral pH in an aqueous dispersion, e.g. having a pH of less than about 11, preferably less than about 9.5. The urea-urethane polymers have an average particle size in the colloidal size range, e.g., less than about 0.1 micron.

The isocyanate-terminated, urethane prepolymers employed in this invention can be made by the reaction of diisocyanates with urethane-forming polyols. At least a

portion of the polyol component has at least one carboxylic acid group



or carboxylate ion group



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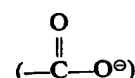
per molecule which is relatively non-reactive with isocyanates. Both the carboxylic acid group and carboxylate ion group are referred to herein as carboxylic groups. Thus, the isocyanate groups of the diisocyanate react preferentially with the hydroxyl groups of the polyol molecule to provide a polymer structure with pendant carboxylic groups available for quarternary salt formation with tertiary amines. The carboxylic group-containing prepolymer is reacted with tertiary amine in an amount which enhances the water-dispersability of the tertiary amine-neutralized, urea-urethane polymers formed in accordance with this invention. The increase in water-dispersability thereby provided is sufficient for the tertiary amine-neutralized polymer to be infinitely dilutable by water, and the amount is adequate for the tertiary amine-neutralized, urea-urethane to be in the form of a stable, colloidal dispersion. Thus, in the aqueous dispersion the amount of ionized carboxylic group

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available from the neutralized carboxylic group in salt form is generally at least about 1.3, e.g., about 1.3 to 6, weight percent of the neutralized, urea-urethane polymer on a non-solvent, non-aqueous basis, i.e., solids basis, preferably at least about 1.6 weight percent, say about 1.6 to 6 weight percent. For example, the amount of carboxylic group-containing polyol reacted may provide unneutralized, prepolymer solids having an acid value of at least about 17, preferably about 20 to 60, on a solids basis. The prepolymers are often in an essentially liquid state, either as the polymer per se or dissolved in a solvent, at ambient temperatures, e.g., about 15° to 45°C., and the prepolymers are generally stable at ambient temperatures in the sense that they will not cure to an insoluble gel for a significant period of time, e.g., for at least about two weeks, unless further contacted with water, polyol, polyamine or other active-hydrogen-containing material. The

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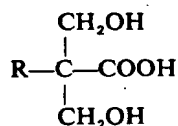
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prepolymers contain a minor amount of free isocyanate groups and generally have a free isocyanate group content of at least about 0.5, say up to about 15, weight percent or somewhat more on a non-solvent basis. For instance, the free isocyanate group content may be at least about 1, and preferably about 1 to 5, weight percent based on the urethane prepolymer solids.

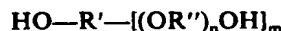
The carboxylic group-containing polyols used in accordance with this invention are advantageously dihydroxy materials, and the dihydroxy-containing alkanolic acids are preferred. The carboxylic group-containing polyol can be reacted, without any significant reaction between the carboxylic groups and the diisocyanate component. Among the polyols which may be employed are those which have relatively unreactive free carboxylic acid groups, for instance, the alkanolic acids having one or two substituents on the alpha carbon atom. The substituent may be, e.g., a hydroxyl or alkyl group, for example, an alkylol group. The polyol has at least one carboxylic group, and generally has 1 to about 3 carboxylic groups, per molecule. The polyols which may conveniently be employed in accordance with this invention frequently have 2 to about 20 or more, preferably 2 to about 10, carbon atoms such as tartaric acid, the α,α -dialkylol alkanolic acids, e.g., having alkylol groups of 1 to about 3 carbon atoms. A preferred group of dihydroxy alkanolic acids are the α,α -dimethylol alkanolic acids which may be represented by the structural formula



wherein R is hydrogen or alkyl, e.g., lower alkyl, say, of 1 to about 8 carbon atoms. The α,α -dimethylol alkanolic acids which may be employed in accordance with this invention include 2,2-dimethylol acetic acid, 2,2-dimethylol propionic acid, 2,2-dimethylol butyric acid and 2,2-dimethylol pentanoic acid. A preferred dihydroxy alkanolic acid is 2,2-dimethylol propionic acid. The carboxylic group-containing polyol may frequently provide at least about 3 to say up to about 90, or more, preferably about 5 to 50, weight percent of the total polyol component in the prepolymer.

Polyols, in addition to the carboxylic group-containing polyol, may be employed in making the prepolymers, and these additional polyols include those having a molecular weight of at least about 400. Generally, the average molecular weight of these additional polyols will not exceed

about 5,000, and is preferably about 400 to 4,000. These additional polyols may comprise up to about 95 weight percent of the total polyol comprising the carboxylic group-containing polyol and additional polyol. Particularly desirable aliphatic polyols are those represented by the formula:



in which R' is a hydrocarbon radical, preferably saturated, and R'' is an alkylene radical of 2 to 4, preferably 3 to 4, carbon atoms. R' preferably has 2 to 12, advantageously 2 to 4, carbon atoms. The letter n represents a number up to about 50, depending on the molecular weight desired, while the letter m is at least say up to 1 to 2 or more, and is preferably 1, i.e., the polyol is a diol. Among the higher molecular weight polyols which may be employed are the polyether polyols of up to about 5,000 or more molecular weight, such as the polyoxyethylene polyols, polyoxypropylene polyols and polyoxybutylene polyols. The latter materials include the straight chain polyoxybutylene glycols often referred to as tetramethyleneether glycols, as well as the branched-chain polyoxybutylene glycols, for instance, made from 1,2- and 2,3-butylene oxides. It is preferred that the polyethers not contain excessive amounts of ether groups since the resulting polymers tend to swell in water.

Other desirable polyols which may be employed include the polyester polyols of up to about 5,000 or more, e.g., about 400 to 4,000 or 5,000, molecular weight which may be derived for instance, from a polyol and a dicarboxylic acid or hydroxy carboxylic acid or lactone. The dicarboxylic acid or hydroxy carboxylic acid may often have from 3 to about 30, preferably 4 to about 12, carbon atoms and may be aliphatic, alicyclic, aromatic or mixed structures of these types. The dicarboxylic acid, hydroxy carboxylic acid, or lactone may be substituted with groups which do not deleteriously affect the production of the desired urea-urethane products. Exemplary dicarboxylic acids and anhydrides which may be employed in this invention are orthophthalic acid, orthophthalic acid anhydride, isophthalic acid, terephthalic acid, adipic acid, cyclohexane-1,4-dicarboxylic acid, succinic acid, succinic acid anhydride, sebacic acid, dimers of olefinically-unsaturated monocarboxylic acids, such as lineolic acid dimer, and their mixtures. Minor amounts of carboxylic acids having three or more carboxylic groups may also be present during formation of the polyester polyols. The hydroxy carboxylic acids which

may be employed as a reactant in providing a hydroxy-terminated polyester polyol include, for instance, hydroxycaproic acid, hydroxybutyric acid, hydroxydecanoic acid and hydroxystearic acid. Useful lactones include caprolactone and butyrolactone. The polyols which may be employed in preparing the polyester polyols are often low molecular weight polyols, e.g., diols having, say, up to about 20 carbon atoms. Exemplary of the polyols which may be employed to prepare polyester polyols are 1,6 - hexanediol, neopentyl glycol, trimethylol propane, ethylene glycol, 1,4 - butanediol and 1,4 - cyclohexane dimethanol.

The polyol component used in making the prepolymers employed in the present invention may contain low molecular weight polyol to enhance the hardness of the urethane films. The low molecular weight polyol may often have a molecular weight of up to, say, about 400, e.g., about 60 to 400, and can contain aliphatic, alicyclic, or aromatic groups. Frequently, the low molecular weight polyol, when employed, is at least about 1, preferably about 2 to 30, weight percent of the overall polyol component. Among the advantageous low molecular weight polyols are those having up to about 20 carbon atoms per molecule, for instance, ethylene glycol, 1,2 - propanediol, 1,3 - propanediol, 1,4 - butanediol, 1,3 - butylene glycol, trimethylol propane, 1,4 - cyclohexane dimethanol, 1,6 - hexanediol, bisphenol A (2,2 - bis(4 - hydroxyphenyl)propane) and hydrogenated bisphenol A (2,2 - bis(4 - hydroxycyclohexyl)propane), and mixtures thereof.

The essentially hydrocarbon diisocyanates which are useful in preparing the prepolymers employed in this invention are preferably the aliphatic and alicyclic diisocyanates. While certain aromatic diisocyanates may be employed as the diisocyanate component, they are generally less preferred in applications in which yellowing due to the effects of ultraviolet light, may be undesirable, or where hydrolytic stability is important. The diisocyanates can contain non-interfering groups, e.g., aliphatic hydrocarbon radicals such as lower alkyl or other groups, having substantially non-reactive hydrogens as determined by the Zerewitinoff test, *J. Am. Chem. Soc.*, 49, 3181 (1927). The diisocyanate often has at least 6 carbon atoms and usually does not have more than about 40 carbon atoms. Diisocyanates of about 8 to 20 carbon atoms in the hydrocarbon group are preferred. Suitable diisocyanates include 2,4 - toluene diisocyanate; 2,6 - toluene diisocyanate; 1,4 - cyclohexane diisocyanate; dicyclohexylmethane 4,4' - diisocyanate; xylene

diisocyanate; 1 - isocyanato - 3 - isocyanatomethyl - 3,5,5 - trimethylcyclohexane; hexamethylene diisocyanate; methylcyclohexyl diisocyanate; and 2,4,4 - trimethylhexylmethylenediisocyanate. The aliphatic and alicyclic diisocyanates which may be employed in this invention generally exhibit good resistance to the degradative effects of ultraviolet light. The polyisocyanate component used to form the prepolymers may contain a portion of polyisocyanates having more than two isocyanate groups per molecule providing the urethane prepolymer compositions are not unduly deleteriously affected.

The polyurethane prepolymer reaction products employed in the present invention can be made by simultaneously reacting an excess of diisocyanate with polyol. Alternatively, the diisocyanate can be reacted with part or all of one or more of the polyols prior to the reaction with the remaining portion of these materials. Stepwise mixing of the diisocyanate with the polyols may be used to enhance temperature control and/or produce a blocked copolymer rather than a random copolymer. The reaction temperatures for making the various urethane prepolymers are often up to about 150°C., with about 50° to 130°C. being preferred. The reaction is preferably continued until there is little, if any, unreacted hydroxyl functionality remaining. Preferably, the free isocyanate content of the prepolymer is about 1 to 5 weight percent of the prepolymer solids. The reaction may be conducted in the presence of a catalyst such as organotin compounds and tertiary amines; however, this is generally not necessary, and it is often preferred to conduct the reaction without a catalyst. As noted above, variations in the nature and amounts of polyol and polyol mixtures used in the preparation of the compositions of this invention can be made to provide polymers exhibiting desired characteristics.

The urethane prepolymers can be prepared in the presence of a solvent which is essentially inert to the reaction. The solvents are generally organic and may be comprised essentially of carbon and hydrogen with or without other elements such as oxygen or nitrogen. While it may not be necessary to employ a solvent during formation of the urethane prepolymer, the use of a solvent may be desirable to maintain the reactants in the liquid state as well as permit better temperature control during the reaction by serving as a heat sink and, if desired, as a refluxing medium. The solvent employed should not contain active hydrogen as determined by the Zerewitinoff test. Solvents which may be employed include dimethylformamide, esters, ethers,

5 keto-esters, ketones, e.g., methyl ethyl ketone and acetone, glycol-ether-esters, chlorinated hydrocarbons, aliphatic and alicyclic hydrocarbon pyrrolidones, e.g.,
10 N - methyl pyrrolidones, hydrogenated furans and aromatic hydrocarbons, and mixtures thereof. The amount of solvent employed, if any, can vary widely. The amount of solvent employed should be
15 sufficient to provide a prepolymer solution having a sufficiently low viscosity to enhance the formation of the urea-urethane polymer dispersion of this invention. Often about 0.01 to 10 parts by weight of solvent,
20 preferably about 0.02 to 2 parts by weight of solvent, per part by weight of the total diisocyanate and polyol in the prepolymer can be used. The presence of a solvent for the urea-urethane polymer, however, is not
25 necessary to provide a stable, infinitely dilutable aqueous dispersion. Often, when solvent is employed during the preparation of the urethane prepolymer and/or the urea-urethane polymer it is desirable to remove at least a portion of the solvent from the aqueous dispersion of polymer.
30 Advantageously, the solvent to be removed from the dispersion has a lower boiling point than water and thus can be removed from the dispersion by, for example, distillation. The removal of the low boiling solvent is desirably conducted under conditions which are not deleterious to the urea-urethane polymer such as vacuum distillation or thin film evaporation conditions. A solvent
35 having a higher boiling point than water such as dimethyl formamide and N - methyl - pyrrolidone, which is a solvent for the urea-urethane polymer may be employed, in which case, the higher boiling solvent is generally retained in the aqueous dispersion of urea-urethane polymer to enhance the coalescence of the urea-urethane polymer particles during film formation.
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The isocyanate-terminated prepolymer contains carboxylic groups. In the urea-urethane aqueous dispersions of the present invention at least a portion of these groups are reacted with amines having at least one salt-forming tertiary amine group, e.g., aliphatic tertiary amine groups, preferably a trialkyl amine, generally having 3 to about 12 carbon atoms, such as trimethyl amine, triethyl amine, methyl diethyl amine, N,N - dimethylethanol amine and tripropyl amine. Thus the alkyl groups of the amine may be substituted with, for instance, hydroxy groups, as in the alkanolamines such as the dialkylmonoalkanol, alkylalkanol and trialkanol amines. Triethyl amine, and N,N - dimethyl ethanol amine are preferred amines. Desirably, the tertiary amine employed is relatively volatile. The tertiary amines react to form quaternary amine salts

of the carboxylic acid groups of the polymer which salts are generally more hydrophilic than the free acid groups. The quaternary amine salts of the carboxylic groups of the urethane prepolymer and the urea-urethanes made therefrom are preferably capable of decomposing during the formation of, e.g., coatings, of the urea-urethanes of this invention with the tertiary amine being volatilized and removed from the coating. Thus, the resulting urea-urethane coatings may be less sensitive to water than the corresponding quaternary amine salt group-containing materials.

The tertiary amine salts of the carboxylic acids are provided in amounts such that the aqueous, neutralized urea-urethane polymer dispersion is infinitely dilutable with water and is a colloidal dispersion. The salt-forming tertiary amine is, therefore, generally provided in a mole ratio to the carboxylic groups of the prepolymer of about 0.3:1 to 1.3:1, preferably about 0.5:1 to 1:1. The neutralized salt of the polymer may have salt groups other than the tertiary amine salt groups present, e.g., a minor amount of alkali metal salt, such as the lithium, sodium, and/or potassium salts, on a molar salt basis. Urea-urethane films containing unduly large amounts of alkali metal salts are generally less water resistant than films prepared from urea-urethane dispersions of more highly tertiary amine-neutralized polymers. Therefore, if the urea-urethane contains alkali metal salt groups such alkali metal salt groups should not be in amount sufficient to unduly detract from the properties of the ultimate film.

The tertiary amine may, for instance, be reacted with urethane prepolymers having free carboxylic acid groups. The tertiary amine is preferably added to the prepolymer in the presence of a sufficient amount of water to form a dispersion of the neutralized prepolymer in the water. The water may conveniently be added in admixture with the tertiary amine. Alternatively, the tertiary amine may be added before the addition of the water. Frequently, the water is provided in a weight ratio to urethane prepolymer solids of about 0.2:1 to 5:1, preferably about 0.5:1 to 3:1, on a total weight basis. A solvent for the prepolymer may also be present when the tertiary amine and water are added to provide a viscosity suitable to facilitate the addition of the tertiary amine and water. Advantageously, the solvent is water-miscible and at least a portion of the solvent is low boiling, i.e., has a lower boiling point than water. Often, the solvent may be provided in a weight ratio to the urethane polymer of at least about 1:5, and generally for economic reasons the

weight ratio of the solvent to the urethane polymer is less than about 5:1.

5 The reaction between the tertiary amine and the carboxylic acid groups of the urethane prepolymer may occur at ambient temperature; however, lower or elevated temperatures of, e.g., about 15° to 50°C. may conveniently be employed. The prepolymer mixture can advantageously be
10 agitated and the addition of the tertiary amine and water conducted over a period of time, e.g., intermittently or continuously for about 0.5 to 30 minutes. If the water, or a portion of the water, of the dispersion is
15 added after the tertiary amine or tertiary amine and water mixture, the prepolymer mixture is advantageously agitated during such water addition to assist in providing the dispersion of the prepolymer in the aqueous
20 mixture. The contact of the isocyanate-terminated urethane prepolymer with water should not be unduly excessive prior to chain extension with polyamine since water is reactive with free isocyanate groups, e.g.,
25 it may be desirable to initiate the addition of the polyamine more or less immediately, say within about 15 minutes or less, after adding water, to avoid undue reaction of the prepolymer with water.

30 The chain extension of the urethane prepolymer is frequently conducted in an aqueous medium such that the dispersion of the urea-urethane polymer in water is directly formed. The polyamines which are
35 employed to provide the urea-urethane product of this invention can be selected from a variety of suitable polyamines. Often the polyamine is an essentially hydrocarbon polyamine having at least 2 amine groups
40 providing reactive hydrogens in accordance with the Zerewitinoff test, e.g., primary and secondary amine groups, and having 1 to about 40 or more carbon atoms, preferably about 2 to 15 carbon atoms. Preferably, the
45 polyamine has at least 2 primary amine groups. The polyamine may contain other substituents which do not have hydrogen atoms as reactive with isocyanate groups as the primary or secondary amine groups. The
50 polyamine may have, for instance, an aromatic, aliphatic or alicyclic structure. Among the useful polyamines are ethylene diamine, propylene diamine, 1,4 - butylene diamine, piperazine, 1,4 -
55 cyclohexyldimethylamine, hexamethylene diamine, trimethylhexamethylene diamine, menthanediamine, 4,4' - diaminodicyclohexylmethane and diethylenetriamine. Preferred polyamines are the alkyl or
60 cycloalkyl diamines, e.g., 1 - amino - 3 - aminomethyl - 3,5,5 - trimethyl cyclohexane and diethylene triamine. The urethane prepolymer can be reacted with one or more of these polyamines to obtain
65 the urea-urethane product.

The amounts of the urethane prepolymer and polyamine reactants and the reaction conditions are generally chosen such that substantially all of the isocyanate content of the prepolymer is reacted on a weight basis
70 with the primary or secondary amine groups; however, a small portion of the isocyanate content may react with the water. Thus, an approximately stoichiometric amount of amine or slightly
75 less is generally used. It is preferred that the polyamine not be in an unduly large excess in the presence of the urethane prepolymer since a lower molecular weight urea-urethane polymer may be formed which is
80 less desirable.

The chain extension can be conducted at elevated, reduced or ambient temperatures. Convenient temperatures are from about 5 to 95°C. or more, preferably from about 10°
85 to about 45°C. Elevated or reduced pressures may be employed, however, the chain extension reaction is normally conducted at approximately ambient pressure. Generally it is desired to continue the reaction until a good yield of the desired urea-urethane polymer is obtained. Preferably, the polyamines employed in the
90 method of this invention react rapidly with the urethane prepolymer such that undue reaction of water with the isocyanate groups is avoided.

The polyamine is preferably gradually added to the reaction medium which contains the urethane prepolymer in order
100 to prevent the occurrence of localized high concentrations of the added reactant which may lead to forming urea-urethanes having an unduly broad molecular weight range. When employing high concentrations of the reactants in the reaction medium it is preferred that the combination of the polyamine and prepolymer be less rapid
105 than when the reactants are less concentrated. For instance, when the reactants are in relatively low concentration in the reaction medium and the medium is well agitated, the polyamine and prepolymer can be quickly combined. Frequently, the rate of
110 addition of the polyamine will be over a period of about 0.5 to 30 minutes. The rate of addition of the polyamine may, in part, depend upon the degree of agitation of the reaction medium and the speed with which the polyamine is dissipated in the reaction medium. The polyamine may be added in essentially undiluted form or in admixture
115 with an organic solvent or with water. Preferably, the polyamine is in an essentially aqueous solution. A convenient weight ratio of water or other solvent to polyamine may be employed and often the weight ratio of water or other solvent to polyamine is about
120 1:1 to 5:1.
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The urea-urethane polymer may have a minor amount of cross-linking and still form a continuous film under normal curing conditions. An unduly large amount of cross-linking, however, is undesirable since the polymer particles may be too stiff to form a continuous film under normal curing conditions. The cross-linking of the urea-urethane polymer can be provided by the use of either or both of at least a trifunctional prepolymer or at least a trifunctional polyamine. The trifunctional or higher prepolymers may be produced from a trifunctional or correspondingly higher polyol and/or polyisocyanate during the formation of the urethane prepolymer from polyol and diisocyanate. Often, the cross-linking polyols are aliphatic and have about 3 to 12, preferably about 3 to 6, carbon atoms, per molecule, although their polyether or polyester polyol derivatives may have significantly higher molecular weights. It is generally preferred, however, that any trifunctional or higher component be provided at least to a major extent by the polyamine since excessively cross-linked urethane prepolymers may be highly viscous and require excessive amounts of solvent to provide a solution of desirable viscosity for further processing or may form an intractable gel which is unsuitable for further processing. A preferred trifunctional polyamine is diethylene triamine.

The urea-urethane polymer which is formed in accordance with the present invention is generally in the lower colloidal particle size range, e.g., having an average particle size up to about 0.1 micron, and the urea-urethane polymer preferably has an average particle size of up to about 0.05 micron, e.g., about 0.001 to 0.05 micron. Colloidal dispersions of the urea-urethane polymer in water may appear essentially or nearly transparent and thus may be essentially in solution-like form. The colloidal particle sizes of the urea-urethane polymers of this invention enhance stability of the polymer dispersions in aqueous compositions and are infinitely-dilutable in aqueous media, even in the absence of a cosolvent. With smaller polymer particles, the tendency to form high gloss films may be increased and the ability of the dispersion to accept pigments is generally enhanced. Colloidal size particles are not readily filtered from the dispersion.

The urea-urethane polymer aqueous dispersions of this invention are advantageously employed as aqueous coating compositions. Frequently, the aqueous compositions have a relatively neutral pH, say, about 6 to 11, preferably about 7 to 9.5. The coating compositions may contain ingredients other than water and the urea-urethane polymer such as a

higher boiling, e.g., slower evaporating than water, solvent for the urea-urethane polymer, particularly solvents which may be miscible with water such as dimethyl formamide, N-methyl pyrrolidone, alkoxyalkanols, alkyl diethers, and carboxylic esters derived from alkoxyalkanols. The higher boiling solvent is advantageously provided in a minor amount sufficient to aid the coalescence of the polymer particles after the bulk of the water has been evaporated. Essentially complete coalescence of the polymer particles tends to provide desirably glossy finishes and enhance physical properties, e.g., strength of the film. Frequently, the slower evaporating solvent is provided in a weight ratio to urea-urethane solids of up to about 1:2, preferably about 1:3. The slower evaporating solvent may be introduced during the formation of the prepolymer or urea-urethane polymer, or it can be added to the aqueous dispersion of the urea-urethane polymer.

The composition may contain other ingredients for coating compositions including plasticizers to modify the properties of the resultant urea-urethane, pigments, colorants, dyes, emulsifying agents, surfactants, thickeners, heat stabilizers, levelling agents, anti-cratering agents, fillers, sedimentation inhibitors and ultraviolet-light absorbers. The additives such as heat stabilizers and ultraviolet-light absorbers, may be intimately dispersed in the reaction mixture and apparently thereby become an integral part of each individual urea-urethane particle when formed. Alternatively, the additive may be introduced after the urea-urethane polymer has been formed, in which case the additive can be incorporated on the surface of the polymer or dispersed in the aqueous medium.

The urea-urethane polymers used in this invention including the higher molecular weight urea-urethane polymers can comprise a large amount of the aqueous composition without the composition having an undesirably high viscosity, and the viscosity of the aqueous dispersion may be lower than that of analogous urea-urethane polymers dissolved in organic solvents. The non-volatile content of the coating compositions of this invention may often range from about 5 to 70, preferably about 10 to 50, weight percent of the composition. The non-volatile content of the compositions may vary depending upon the nature of the coating and the manner in which the coating is to be applied, e.g., by spraying, brushing, or transfer coating. The aqueous compositions are infinitely dilutable with water. Advantageously, water can be employed to thin the compositions, and the

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washing of application equipment and splatterings is facilitated.

The aqueous dispersions of the urea-urethane polymers of this invention can also be used in applications other than coatings, e.g., in casting to form thin films and as adhesives. The film-type products generally have a thickness of up to about 100 mils or more, and often the coating compositions have a thickness of up to about 10 mils. The urea-urethane dispersions can be formed into various materials or articles of greater cross-sectional dimensions, and can be employed in the various ways known in the art for utilization of these types of materials. The coatings, due to the use of water in the compositions, can be dried at temperatures of, say, about 10°C. or more. Advantageously, relatively low temperatures can be employed, however, elevated temperatures may also be used, e.g., temperatures of up to about 350°C. or more to accelerate removal of water and organic solvent, if present.

The invention will be illustrated further by the following examples. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

A mixture of 148 parts 2,2 - dimethylol-propionic acid, 615 parts melted polytetramethylene ether glycol (about 2,000 molecular weight, hydroxyl number 56.7), and 221 parts dimethylformamide is prepared, and the ingredients are blended under nitrogen for about one-half hour. To the mixture which is being agitated is added 485 parts of 4,4' - methylene bis(cyclohexyl-isocyanate), and the mixture is subsequently heated to 85°-90°C. under a nitrogen blanket for about four hours to form an isocyanate-terminated urethane prepolymer. The prepolymer is cooled and then diluted with 1,029 parts acetone. A diluted isocyanate-terminated prepolymer solution is obtained having a free NCO content of 1.3 percent by weight, an acid value of 25.1, a non-volatile content of 50.9 percent by weight, and a viscosity of about 7 Stokes.

One-thousand parts of the prepolymer is charged to a reaction vessel and agitated under a nitrogen blanket. A mixture of 27 parts triethylamine and 773 parts water is then gradually added to the agitating prepolymer over a ten minute period, and the temperature is maintained between 25° to 31°C. Within one to two minutes after the completion of the addition of the triethylamine and water, a mixture of 26 parts 1 - amino - 3 - aminomethyl - 3,5,5 - trimethylcyclohexane (isophorone diamine) and 104 parts water is gradually added to the prepolymer dispersion over a four to five

minute period, and the temperature is maintained between 31° to 35°C. to form a dispersed, colloidal-sized urea-urethane polymer. The acetone is then distilled from the dispersion to yield a stable aqueous colloidal polyurea-urethane ionomer dispersion with the following analysis: non-volatile content of 36.6 percent by weight, pH of 7.4, and a viscosity of about 3 Stokes. The product contains less than 6 percent dimethylformamide by weight and is infinitely dilutable with water. The colloidal dispersion is only slightly opaque and films from this product are of very high gloss and have a Sward hardness of 34. The polymer is an elastomer exhibiting an ultimate tensile strength of about 4,000 psi and elongation at break of about 360 percent. The films have very good resistance to water spotting.

EXAMPLE 2

A mixture of 72 parts 2,2 - dimethylol-propionic acid, 845 parts melted polytetramethylene ether glycol (about 2,000 molecular weight, hydroxyl number 56.7), and 211 parts dimethylformamide is prepared, and the ingredients are blended under nitrogen for about one-half hour. To the mixture which is being agitated is added 274 parts of trimethyl-hexamethylene diisocyanate and the mixture is subsequently heated to 85° to 90°C. under a nitrogen blanket for about four hours. The resulting isocyanate-terminated urethane prepolymer is cooled and then diluted with 1,098 parts acetone. A diluted, isocyanate-terminated prepolymer solution is obtained having a free NCO content of 1.1 percent by weight, an acid value 11.1, a non-volatile content of 48.6 percent by weight, and a viscosity of about 2 Stokes.

One-thousand-six-hundred-fifty-four parts of the prepolymer is charged to a reaction vessel and agitated under a nitrogen blanket. Twenty-three parts of dimethylformamide is then blended with the prepolymer. A mixture of 35 parts triethylamine and 1,112 parts water is then gradually added to the agitating prepolymer over a ten minute period, and the temperature is maintained between 25° to 30°C. Within one to two minutes after the completion of the addition of the triethylamine and water, a mixture of 35 parts 1 - amino - 3 - aminomethyl - 3,5,5 - trimethyl-cyclohexane and 153 parts water is gradually added to the prepolymer dispersion over a five minute period, and the temperature is maintained between 30° to 35°C. to form a dispersed, colloidal-sized urea-urethane polymer. The acetone is then distilled from the dispersion to yield a very stable aqueous colloidal polyurea-urethane ionomer dispersion with the following analysis: non-volatile content of 38.8

percent by weight, pH of 8.3, and a viscosity of about 54 Stokes. The product contains less than 7 percent dimethylformamide by weight and is infinitely dilutable with water. The colloidal dispersion is only slightly opaque and films from this product are of very high gloss and have a Sward hardness of 2. The films are elastomeric and exhibit an ultimate tensile strength of about 2,000 psi and an elongation at break of about 1,000 percent. The films have very good resistance to water spotting.

EXAMPLE 3

A mixture of 145 parts, 2,2 - dimethylol-propionic acid, 1,740 parts polyoxypropylene polyol (about 2,000 molecular weight, hydroxyl number 56.0) and 237 parts dimethylformamide is formed, and the ingredients are blended under nitrogen for about one-half hour. To the mixture which is undergoing agitation is added 559 parts of trimethylhexamethylene diisocyanate and the mixture is subsequently heated to 85° to 90°C. under a nitrogen blanket for about four hours to provide an isocyanate-terminated urethane prepolymer. The prepolymer is cooled and then diluted with 500 parts acetone. A diluted, isocyanate-terminated prepolymer solution is obtained having a free NCO content of 1.9 percent by weight, an acid value of 18.5, a non-volatile content of 74.7 percent by weight, and a viscosity of about 6 Stokes.

Six-hundred-thirteen parts of the prepolymer is charged to a reaction vessel and agitated under a nitrogen blanket. A mixture of 16 parts triethylamine and 771 parts water is then gradually added to the agitating prepolymer over a ten minute period, and the temperature is maintained between 25° to 33°C. Within one to two minutes after the completion of the addition of the triethylamine and water, a mixture of 24 parts 1 - amino - 3 - aminomethyl - 3,5,5 - trimethylcyclohexane and 80 parts water is gradually added to the prepolymer dispersion over a four to five minute period, and the temperature is maintained between 33° to 37°C. The acetone is then distilled from the dispersion to yield a very stable aqueous colloidal polyurea-urethane ionomer dispersion with the following analysis: non-volatile content of 37.6 percent by weight, pH of 8.1, and a viscosity of about 2 Stokes. The product contains less than 4 percent dimethylformamide by weight and is infinitely dilutable with water. The colloidal dispersion is only slightly opaque and films from this product are of very high gloss. The polymer is an elastomer exhibiting an ultimate tensile strength of about 200 psi, elongation at break of about 900 percent, and a Shore hardness of A50.

The films have good resistance to water spotting.

EXAMPLE 4

A mixture of 148 parts dimethylol-propionic acid, 615 parts melted polytetramethylene ether glycol (about 2,000 molecular weight, hydroxyl number 56.7), and 417 parts of methyl ethyl ketone is prepared, and the ingredients are blended under nitrogen for about one-half hour. To the mixture which is undergoing agitation is added 485 parts of 4,4' - methylene bis(cyclohexyl isocyanate). The mixture is subsequently heated to 85° to 90°C. under a nitrogen blanket for about four hours to form an isocyanate-terminated urethane prepolymer. The prepolymer is cooled and then diluted with 833 parts of acetone. A diluted, isocyanate-terminated prepolymer solution is obtained having a free NCO content of 1.2 percent by weight, an acid value of 24.3, a non-volatile content of 49.9 percent by weight, and a viscosity of about 12 Stokes.

One-thousand-five-hundred-fifty parts of the prepolymer is charged to a reaction vessel and agitated under a nitrogen blanket. A mixture of 42 parts triethylamine and 1,202 parts water is then gradually added to the agitating prepolymer over a ten minute period, and the temperature is maintained between 25° to 28°C. Within one to two minutes after the completion of the addition of the triethylamine and water, a mixture of 38 parts 1 - amino - 3 - aminomethyl - 3,5,5 - trimethylcyclohexane and 162 parts water is gradually added to the prepolymer dispersion over a four to five minute period, and the temperature is maintained between 28° to 32°C. The acetone and methyl ethyl ketone are then distilled from the dispersion to yield a very stable aqueous colloidal polyurea-urethane ionomer dispersion essentially free from organic solvent. The product has the following analysis: non-volatile content of 38.6 percent by weight, pH of 7.2, and viscosity of about 22 Stokes. The product is infinitely dilutable with water. The colloidal dispersion is only slightly opaque and films from this product are of very high gloss. A 3 mil wet film cured at 90°C. for a half hour exhibits extremely tough, yet elastomeric, properties. A 3 mil wet film cured at 25°C. overnight contains a small amount of cracking and is brittle. If a low level of a slow evaporating organic solvent is added to the organic solvent-free vehicle, then a 25°C. cured film does not crack and elastomeric film properties are again obtained. The films have very good resistance to water spotting.

EXAMPLE 5

A mixture of 105 parts 2,2 - dimethylol-

propionic acid, 35 parts hydrogenated bisphenol A, 661 parts polyoxypropylene polyol (about 2,000 molecular weight, hydroxyl number 56.0), and 220 parts dimethylformamide is prepared, and the ingredients are blended under nitrogen for about one-half hour. To the mixture which is undergoing agitation is added 445 parts of 4,4' - methylene bis(cyclohexyl isocyanate). The resultant mixture is heated to 85° to 90°C. under a nitrogen blanket for about four hours and an isocyanate-terminated urethane prepolymer forms. The prepolymer is cooled and then diluted with 1029 parts acetone. A diluted, isocyanate-terminated prepolymer solution is obtained having a free NCO content of 1.4 percent by weight, an acid value of 18.8, a non-volatile content of 51.7 percent by weight, and a viscosity of about 1 Stoke.

One-thousand parts of the prepolymer is charged to a reaction vessel and agitated under a nitrogen blanket. A mixture of 26 parts triethylamine and 752 parts water is then gradually added to the agitating prepolymer over a ten minute period, and the temperature is maintained between 25° to 32°C. Within one to two minutes after the completion of the addition of the triethylamine and water, a mixture of 28 parts 1 - amino - 3 - aminomethyl - 3,5,5 - trimethylcyclohexane and 114 parts water is gradually added to the prepolymer dispersion over a four to five minute period. The reaction temperature is maintained between 32° to 36°C. The acetone is then distilled from the dispersion to yield a very stable aqueous colloidal urea-urethane ionomer dispersion with the following analysis: non-volatile content of 37 percent by weight, pH of 7.6, a viscosity of about 8 Stokes. The product contains less than 5.7 percent dimethylformamide by weight and is infinitely dilutable with water. Films from this product are of very high gloss and have a Sward hardness of 18. The films are elastomers exhibiting an ultimate tensile strength of about 2,000 psi and an elongation at break of about 300 percent. The films have very good resistance to water spotting.

EXAMPLE 6

A mixture of 150 parts 2,2 - dimethylol-propionic acid, 60 parts hydrogenated bisphenol A, 364 parts polyoxypropylene polyol (about 440 molecular weight, hydroxyl number 254), and 225 parts dimethylformamide is prepared, and the ingredients are blended under nitrogen for about one-half hour. To the mixture which is undergoing agitation is added 697 parts of 4,4' - methylene bis(cyclohexyl isocyanate). The resultant mixture is heated to 85° to 90°C. under a nitrogen blanket for about

four hours to provide an isocyanate-terminated urethane prepolymer. The prepolymer is cooled and then diluted with 1050 parts acetone. The diluted, isocyanate-terminated prepolymer solution which is obtained has a free NCO content of 1.0 percent by weight, an acid value of 25.4, a non-volatile content of 52.5 percent by weight, and a viscosity of about 7 Stokes.

One-thousand parts of the prepolymer is charged to a reaction vessel and agitated under a nitrogen blanket. Forty-nine parts of acetone is then blended with the prepolymer. A mixture of 37 parts triethylamine and 803 parts water is then gradually added to the agitating prepolymer over a ten minute period, and the temperature is maintained between 25° to 32°C. Within one to two minutes after the completion of the addition of the triethylamine and water, a mixture of 19 parts 1 - amino - 3 - aminomethyl - 3,5,5 - trimethylcyclohexane and 77 parts water is gradually added to the prepolymer dispersion over a four to five minute period, and the temperature is maintained between 32° to 34°C. Fifty-eight parts of water is then added to the dispersion. The acetone is then distilled from the dispersion to yield a very stable aqueous colloidal urea-urethane ionomer dispersion with the following analysis: non-volatile content of 34.0 percent by weight, pH of 7.7, and a viscosity of about 24 Stokes. The product contains less than 5.8 percent dimethylformamide by weight and is infinitely dilutable with water. Films from this product are non-elastomeric and are of very high gloss and have a Sward hardness of 44. The films have excellent resistance to water spotting.

EXAMPLE 7

A mixture of 176 parts 2,2 - dimethylol-propionic acid, 75 parts hydrogenated bisphenol A, 322 parts polytetramethylene ether glycol (about 620 molecular weight, hydroxyl number 179.8), and 221 parts dimethylformamide is prepared, and the ingredients are blended under nitrogen for about one-half hour. To the mixture which is undergoing agitation is added 675 parts of 4,4' - methylene bis(cyclohexyl isocyanate). The resultant mixture is heated to 85° to 90°C. under a nitrogen blanket for about four hours to provide an isocyanate-terminated urethane prepolymer. The prepolymer is cooled and then diluted with 1029 parts acetone. A diluted, isocyanate-terminated prepolymer solution is obtained having a free NCO content of 1.1 percent by weight, an acid value of 31.7, a non-volatile content of 55.9 percent by weight, and a viscosity of about 40 Stokes.

One thousand parts of the prepolymer is charged to the reaction vessel and agitated

under a nitrogen blanket. One-hundred-eighteen parts of acetone is then blended with the prepolymer. A mixture of 47 parts triethylamine and 846 parts water is then gradually added to the agitating prepolymer over a ten minute period, and the temperature is maintained between 25° to 35°C. Within one to two minutes after the completion of the addition of the triethylamine and water, a mixture of 22 parts 1 - amino - 3 - aminomethyl - 3,5,5 - trimethylcyclohexane and 87 parts water is gradually added to the prepolymer dispersion over a four to five minute period. The reaction temperature is maintained between 35° to 37°C. Twenty-eight parts water is then added to the dispersion. The acetone is then distilled from the dispersion to yield a very stable aqueous colloidal urea-urethane ionomer dispersion with the following analysis: non-volatile content of 34.4 percent by weight, pH of 7.5, and a viscosity of about 127 Stokes. The product contains less than 5.8 percent dimethylformamide by weight and is infinitely dilutable with water. Films from this product are non-elastomeric and are of very high gloss and have a Sward hardness of 58. The films have excellent resistance to water spotting.

EXAMPLE 8

A mixture of 151 parts 2,2 - dimethylolpropionic acid, 60 parts hydrogenated bisphenol A, 364 parts polyoxypropylene polyol (about 440 molecular weight, hydroxyl number 254), and 425 parts of methyl ethyl ketone is prepared, and the ingredients are blended under nitrogen for about one-half hour. To the mixture which is undergoing agitation is added 697 parts of 4,4' - methylene bis(cyclohexyl isocyanate). The mixture is subsequently heated to 85° to 90°C. under a nitrogen blanket for about four hours to provide an isocyanate-terminated urethane prepolymer. The prepolymer is cooled and then diluted with 850 parts acetone. A diluted, isocyanate-terminated prepolymer solution is obtained having a free NCO content of 1.3 percent by weight, an acid value of 25.2, non-volatile content of 50.0 percent by weight, and a viscosity of about 5 Stokes.

One-thousand parts of the prepolymer is charged to the reaction vessel and agitated under a nitrogen blanket. A mixture of 36 parts triethylamine and 942 parts water is then added gradually to the agitating prepolymer over a ten minute period, and the temperature is maintained between 25° to 30°C. Within one to two minutes after the completion of the addition of the triethylamine and water, a mixture of 26 parts 1 - amino - 3 - amino - methyl -

3,5,5 - trimethylcyclohexane and 85 parts water is gradually added to the prepolymer dispersion over a four to five minute period. The reaction temperature is maintained between 30° to 34°C. The acetone and methyl ethyl ketone are then distilled from the dispersion to yield a very stable aqueous colloidal polyurethane ionomer dispersion with a non-volatile content of 34.2 percent by weight. This organic solvent-free vehicle is infinitely dilutable with water. This vehicle is then reduced to 31.9 percent non-volatile with Cellosolve acetate with the following analysis: pH of 7.6 and a viscosity of about 18 Stokes. The Cellosolve acetate-diluted vehicle yielded films of high gloss with no cracking and a Sward hardness of 70. (Cellosolve is a registered Trade Mark.) The films have very good resistance to water spotting.

EXAMPLE 9

A mixture of 72 parts 2,2 - dimethylolpropionic acid, 845 parts melted polytetramethylene ether glycol (about 2,000 molecular weight, hydroxyl number 56.7), and 210 parts methyl ethyl ketone is prepared, and the ingredients are blended under nitrogen for about one-half hour. To the mixture which is being agitated is added 274 parts of trimethylhexamethylene diisocyanate, and the mixture is subsequently heated to 85° to 90°C. under a nitrogen blanket for about three hours to form an isocyanate-terminated urethane prepolymer. The prepolymer is cooled and then diluted with 558 parts acetone. A diluted, isocyanate-terminated urethane prepolymer solution is obtained having a free NCO content of 1.1 percent by weight, an acid value of 16.2, a non-volatile content of 62 percent by weight, and a viscosity of about 43 Stokes.

One-thousand-four-hundred-thirteen parts of the prepolymer is charged to a reaction vessel and agitated under a nitrogen blanket. A mixture of 34 parts N,N - dimethylethanolamine and 1,390 parts water is then gradually added to the agitating prepolymer over a ten minute period, and the temperature is maintained between 29° to 32°C. Within one to two minutes after the completion of the addition of the N,N - dimethylethanolamine and water, a mixture of 15 parts 1 - amino - 3 - amino - methyl - 3,5,5 - trimethylcyclohexane and 6 parts diethylenetriamine (said mixture having about 2—4 amine nitrogen atoms having active hydrogen, per average molecule) and 141 parts water is gradually added to the prepolymer dispersion over a four to five minute period, and the temperature is maintained between 32° to 35°C. to form a colloiddally dispersed urea-urethane polymer. The acetone and methyl

ethyl ketone are then distilled from the dispersion to yield a very stable, essentially organic solvent-free aqueous colloidal polyurea-urethane ionomer dispersion with the following analysis: non-volatile content of 39 percent by weight, pH of 9.2, and a viscosity of about 113 Stokes. The colloidal dispersion is only slightly opaque and is infinitely dilutable with water. Films from this product can be cured under ambient conditions and are of very high gloss and have a Shore hardness of A55. The polymer is an elastomer exhibiting an ultimate tensile strength of about 1,200 psi and elongation at break of about 900 percent. The films have very good resistance to water spotting.

EXAMPLE 10

A mixture of 148 parts 2,2 - dimethylol-propionic acid, 615 parts melted polytetramethylene ether glycol (about 2,000 molecular weight, hydroxyl number 56.7), and 536 parts methyl ethyl ketone is prepared, and the ingredients are blended under nitrogen for about one-half hour. To the mixture which is being agitated is added 485 parts 4,4' - methylene bis(cyclohexyl isocyanate), and the mixture is subsequently heated to 85° to 90°C. under a nitrogen blanket for about four hours to form an isocyanate-terminated urethane prepolymer. The prepolymer is cooled and then diluted with 441 parts acetone. A diluted, isocyanate-terminated urethane prepolymer solution is obtained having a free NCO content of 1.6 percent by weight, an acid value of 30.8, a non-volatile content of 57 percent by weight, and a viscosity of about 21 Stokes.

One-thousand-two-hundred-sixty-eight parts of the prepolymer is charged to a reaction vessel and agitated under a reaction vessel and agitated under a nitrogen blanket. A mixture of 56 parts N, N - dimethylethanolamine and 1,385 parts water is then gradually added to the agitating prepolymer over a ten minute period, and the temperature is maintained between 30° to 33°C. Within one to two minutes after the completion of the addition of the N, N - dimethylethanolamine and water, a mixture of 20 parts 1 - amino - 3 - aminomethyl - 3,5,5 - trimethylcyclohexane and 8 parts diethylenetriamine (said mixture having about 2.4 amine nitrogen atoms having active hydrogen, per average molecule) and 163 parts water is gradually added to the prepolymer dispersion over a four to five minute period, and the temperature is maintained between 33° to 36°C to form a colloiddally dispersed urea-urethane polymer. The acetone and methyl ethyl ketone are then distilled from the dispersion to yield a very stable, essentially organic solvent-free, aqueous

colloidal polyurea-urethane ionomer dispersion with the following analysis: non-volatile content of 32 percent by weight, pH of 9.1, and a viscosity of about 214 Stokes. The colloidal dispersion has an almost perfectly clear appearance and is infinitely dilutable with water. Films from this product can be cured under ambient conditions to yield very high gloss films, and optimum physical properties are attained when the films are cured at elevated temperatures. Twenty-five mil dry films cured at 70°C. overnight attain a Shore hardness of D 70 and exhibit an ultimate tensile strength of about 5,000 psi and elongation at break of about 360 percent. A 3 mil wet film attains its maximum physical properties when cured at 90°C. for less than one-half hour. The heat cured films have very good resistance to water spotting.

EXAMPLE 11

A mixture of 74 parts 2,2 - dimethylol-propionic acid, 740 parts of neopentyl glycol adipate polyester (about 1100 molecular weight, hydroxyl number 101.1) and 221 parts methyl ethyl ketone is prepared, and the ingredients are blended under nitrogen for about one-half hour. To the mixture which is being agitated is added 434 parts 4,4' - methylene bis(cyclohexyl isocyanate), and the mixture is subsequently heated to 85° to 90°C. under a nitrogen blanket for about three hours to form an isocyanate-terminated urethane prepolymer. The prepolymer is cooled and then diluted with 613 parts acetone. A diluted, isocyanate-terminated urethane prepolymer solution is obtained having a free NCO content of 1.7 percent by weight, an acid value of 16.1, a non-volatile content of 59 percent by weight, and a viscosity of about 3 Stokes. Eight-hundred parts of the prepolymer is charged to a reaction vessel and agitated under a nitrogen blanket. A mixture of 18 parts N, N - dimethylethanolamine and 786 parts water is then gradually added to the agitating prepolymer over a ten minute period, and the temperature is maintained between 25° to 31°C. Within one to two minutes after the completion of the addition of the N, N - dimethylethanolamine and water, a mixture of 9 parts 1 - amino - 3 - aminomethyl - 3,5,5 - trimethylcyclohexane and 4 parts diethylene triamine (said mixture having about 2.4 amine nitrogen atoms having active hydrogen, per average molecule) and 112 parts water is gradually added to the prepolymer dispersion over a four to five minute period, and the temperature is maintained between 31° to 34°C. to form a colloiddally dispersed urea-urethane polymer. The acetone and methyl ethyl ketone are then distilled from the dispersion to yield a stable, essentially

organic solvent-free, aqueous colloidal polyurea-urethane ionomer dispersion with the following analysis: non-volatile content of 34 percent by weight, pH of 8.4, and a viscosity of about 164 Stokes. The colloidal dispersion is only slightly opaque and is infinitely dilutable with water. Films from this product can be cured under ambient conditions to yield very high gloss films but optimum physical properties are attained when the films are cured at elevated temperatures. The polymer is a tough elastomeric material.

Examples 9, 10 and 11 illustrate the utilization of polyamines having an average of substantially greater than 2 amine nitrogen atoms having active hydrogen, per molecule of polyamine.

WHAT WE CLAIM IS:—

1. An aqueous, colloidal dispersion of a urea-urethane polymer, said polymer consisting essentially of the reaction product of a polyamine and a tertiary amine salt of a carboxylic-group containing, isocyanate-terminated, urethane prepolymer derived from a polyisocyanate selected from aliphatic diisocyanates, alicyclic diisocyanates, toluene diisocyanate and xylene diisocyanate, the tertiary amine salt content of said urea-urethane polymer being sufficient to provide an aqueous colloidal dispersion of said urea-urethane polymer which is infinitely dilutable with water.
2. An aqueous dispersion according to claim 1, wherein the carboxylic group content of said urea-urethane polymer in tertiary amine salt form is 1.3 to 6 weight percent on a solids basis.
3. An aqueous dispersion according to claim 1 or claim 2, wherein the tertiary amine salt comprises a trialkyl amine salt.
4. An aqueous dispersion according to claim 3, wherein the trialkyl amine salt comprises the triethylamine salt.
5. An aqueous dispersion according to claim 1 or claim 2, wherein the tertiary amine salt comprises a dialkyl monoalkanol amine salt.
6. An aqueous dispersion according to claim 5, wherein the dialkyl monoalkanol amine salt comprises the N,N - dimethyl ethanol amine salt.
7. An aqueous dispersion according to any one of claims 1 to 6, wherein said prepolymer has been prepared from a polyol comprising a dihydroxy alkanolic acid.
8. An aqueous dispersion according to claim 7, wherein said polyol comprises a dihydroxy alkanolic acid and a polyether or polyester polyol.
9. An aqueous dispersion according to claim 8, wherein said polyether or polyester

polyol has a molecular weight of 400 to 5,000 and comprises up to 95 weight percent of said polyol comprising a dihydroxy alkanolic acid and a polyether or polyester polyol.

10. An aqueous dispersion according to any one of claims 7 to 9, wherein said dihydroxy alkanolic acid comprises an α,α - dialkylol alkanolic acid.

11. An aqueous dispersion according to claim 10, wherein the α,α - dialkylol alkanolic acid comprises 2,2 - dimethylolpropionic acid.

12. An aqueous dispersion according to any one of claims 7 to 11, wherein said polyol further comprises a polyol having a molecular weight of up to 400 in an amount sufficient to increase the hardness of said urea-urethane polymer.

13. An aqueous dispersion according to claim 12, wherein said low molecular weight polyol is hydrogenated bisphenol A.

14. An aqueous dispersion according to any one of claims 1 to 13, wherein the isocyanate-terminated prepolymer has an acid value of at least 17 on a solids basis.

15. An aqueous dispersion according to any one of Claims 1 to 14, wherein the polyamine comprises 1 - amino - 3 - aminomethyl - 3,5,5 - trimethylcyclohexane.

16. An aqueous dispersion according to any one of claims 1 to 15, wherein the polyamine comprises diethylene triamine.

17. An aqueous dispersion according to any one of claims 1 to 16, containing a sufficient amount of organic solvent for the urea-urethane polymer which is slower evaporating than water to enhance the coalescence of the urea-urethane polymer particles.

18. An aqueous dispersion according to any one of the preceding claims, wherein the polyamine comprises triamine, or both diamine and triamine.

19. An aqueous dispersion according to claim 18, wherein enough triamine is present to provide some cross-linking within the urea-urethane polymer, said polyamine components having at least two primary or secondary amine groups reactive with isocyanate groups and said polyamine having an average of from substantially greater than 2 to 3 amine nitrogen atoms having active hydrogen, per molecule of polyamine.

20. An aqueous dispersion according to claim 18 or 19, wherein the urea-urethane polymer is the reaction product of the urethane prepolymer and an approximately stoichiometric amount of polyamine consisting essentially of diamine and enough triamine to provide some cross-linking within the urea-urethane polymer, and wherein said polyamine components have at

- least two primary amine groups reactive with isocyanate groups, said polyamine having an average of from about 2.4 to 3 amine nitrogen atoms having active hydrogen, per molecule of polyamine.
21. An aqueous dispersion according to any one of claims 1 to 20 in which said polyisocyanate consists essentially of aliphatic or alicyclic diisocyanate.
22. An aqueous dispersion according to claim 21 in which said polyisocyanate consists essentially of dicyclohexylmethane diisocyanate or 1 - isocyanato - 3 - isocyanatomethyl - 3,5,5 - trimethyl cyclohexane.
23. An aqueous colloidal dispersion of a urea-urethane polymer substantially as herein described and exemplified with reference to any one of Examples 1 to 11.
24. A method for preparing an infinitely water-dilutable, aqueous dispersion of a urea-urethane polymer comprising providing an aqueous dispersion of a tertiary amine salt of a carboxylic group-containing, isocyanate-terminated, urethane prepolymer derived from a polyisocyanate selected from aliphatic diisocyanates, alicyclic diisocyanates, toluene diisocyanate and xylene diisocyanate, by adding a tertiary amine and water to said prepolymer to form an aqueous dispersion of the prepolymer, and adding a polyamine to said aqueous dispersion to extend the isocyanate-terminated urethane prepolymer and provide a colloidal dispersion of urea-urethane polymer in the aqueous medium.
25. A method according to claim 24, wherein the weight ratio of prepolymer to water is 0.2:1 to 5:1.
26. A method according to claim 24 or claim 25, wherein the prepolymer is dissolved in a water-miscible solvent when said, tertiary amine and water are added, said solvent being in an amount sufficient to provide a viscosity suitable to facilitate the addition of the tertiary amine and water.
27. A method according to claim 26, wherein at least a portion of said solvent has a lower boiling point than water and is removed from said dispersion after formation of said urea-urethane polymer dispersion.
28. A method according to claim 26 or claim 27, wherein said solvent comprises acetone.
29. A method according to claim 26 or claim 27, wherein said solvent comprises methyl ethyl ketone.
30. A method according to any one of claims 24 to 29 wherein the polyol component of said prepolymer comprises an α,α - dialkylol alkanoic acid.
31. A method according to claim 30, wherein the α,α - dialkylol alkanoic acid comprises 2,2 - dimethylolpropionic acid.
32. A method according to claim 30 or claim 31, wherein the polyol component further comprises a polyether or polyester polyol having a molecular weight of 400 to 5,000.
33. A method according to claim 32, wherein said polyol further comprises a polyol having a molecular weight of up to 400 in an amount sufficient to increase the hardness of said urea-urethane polymer when used.
34. A method according to any one of claims 24 to 33, wherein said tertiary amine comprises a trialkyl amine.
35. A method according to claim 34, wherein said trialkyl amine comprises triethylamine.
36. A method according to any one of claims 24 to 33, wherein the tertiary amine comprises a dialkyl monoalkanol amine.
37. A method according to claim 36, wherein said dialkyl monoalkanol amine is N,N - dimethyl ethanol amine.
38. A method according to any one of claims 24 to 37, wherein the polyamine comprises 1 - amino - 3 - aminomethyl - 3,5,5 - trimethyl-cyclohexane.
39. A method according to any one of claims 24 to 38, wherein the polyamine comprises diethylene triamine.
40. A method according to any one of claims 24 to 39, wherein the polyamine used to extend the prepolymer comprises triamine, or both diamine and triamine.
41. A method according to claim 40, wherein enough triamine is present to provide some cross-linking within the urea-urethane polymer formed, said polyamine components have at least two primary or secondary amine groups and said polyamine has an average of from substantially greater than 2 to 3 amine nitrogen atoms having active hydrogen, per molecule or polyamine.
42. A method according to claim 40 or 41, wherein the polyamine used to extend the prepolymer consists essentially of diamine and enough triamine to provide some cross-linking within the urea-urethane polymer formed and wherein said polyamine has an average of from about 2.5 to 3 amine nitrogen atoms having active hydrogen, per molecule of polyamine.
43. A method according to any one of claims 24 to 42, in which said polyisocyanate consists essentially of aliphatic or alicyclic diisocyanate.
44. A method according to claim 43, in which said polyisocyanate consists essentially of dicyclohexylmethane diisocyanate or 1 - isocyanato - 3 - isocyanatomethyl - 3,5,5 - trimethyl-cyclohexane.

5 45. A method for preparing an infinitely water-dilutable, aqueous, colloidal dispersion of a urea-urethane polymer conducted substantially as herein described and exemplified with reference to any one of Examples 1 to 11.

10 46. An infinitely water-dilutable, aqueous colloidal dispersion of a urea-urethane polymer whenever prepared by a method according to any one of claims 24 to 44.

47. Coating compositions made using a dispersion according to any one of claims 1 to 23 or 46.

48. Water resistant coatings made using a dispersion according to any one of claims 1 to 23 or 46 or a coating composition according to claim 47.

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